(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
3 December 2015 (03.12.2015)

WIPO | PCT

(10) International Publication Number
WO 2015/181122 A1

(51) International Patent Classification:
C10L 1/04 (2006.01) *C10M 105/04* (2006.01)

(21) International Application Number:
PCT/EP2015/061514

(22) International Filing Date:
26 May 2015 (26.05.2015)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
14170223.3 28 May 2014 (28.05.2014) EP

(71) Applicant *(for all designated States except US)*: **SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.** [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR The Hague (NL).

(71) Applicant *(for US only)*: **SHELL OIL COMPANY** [US/US]; PO Box 2463, One Shell Plaza, Houston, Texas 77252-2463 (US).

(72) Inventors: **MORSINK, Johannes Bernardus Wilhelmus**; Grasweg 31, NL-1031HW Amsterdam (NL). **TURFBOER, Johannes**; Grasweg 31, NL-1031HW Amsterdam (NL). **WIERSMA, Rendert Jan**; Grasweg 31, NL-1031HW Amsterdam (NL). **WINTER, Ferry**; Grasweg 31, NL-1031 HW Amsterdam (NL).

(74) Agent: **MATTHEZING, Robert Maarten**; PO Box 384, NL-2501 CJ The Hague (NL).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

Published:

— *with international search report (Art. 21(3))*

WO 2015/181122 A1

(54) Title: FISCHER-TROPSCH GASOIL FRACTION

(57) Abstract: The present invention provides a Fischer-Tropsch gasoil fraction having an initial boiling point of at least 200°C and a final boiling point of at most 300°C. In another aspect the present invention provides a composition and the use of a Fischer-Tropsch gasoil fraction according to the invention.

FISCHER-TROPSCH GASOIL FRACTION

The present invention relates to a Fischer-Tropsch gasoil fraction, electrical discharge machining fluids compositions comprising the Fischer-Tropsch gasoil fraction, and use of the Fischer-Tropsch gasoil fraction.

Fischer-Tropsch derived gasoils may be obtained by various processes. A Fischer-Tropsch derived gasoil is obtained using the so-called Fischer-Tropsch process. A Fischer-Tropsch process produces a range of hydrocarbon products, including naphtha, gasoil, base oil and other products. The gasoil product is also referred to as the full-range Fischer-Tropsch derived gasoil. An example of such process producing a Fischer-Tropsch derived gasoil is disclosed in WO 02/070628.

In US5906727, a Fischer-Tropsch derived solvent based on a full-range Fischer-Tropsch derived gasoil is disclosed with a boiling range from approximately 160 to 370°C.

There is a need in the art for Fischer-Tropsch gasoil fractions that have a more narrow boiling point range compared to the solvent disclosed in US5906727.

It has now surprisingly been found that specific Fischer-Tropsch gasoil fractions of the full-range Fischer-Tropsch derived gasoil can be advantageously used in electrical discharge machining fluids applications.

To this end, the present invention provides a Fischer-Tropsch gasoil fraction having an initial boiling point of at least 200°C and a final boiling point of at most 300°C.

An advantage of the present invention is that the Fischer-Tropsch gasoil fraction has surprisingly a low viscosity while having a high flash point, which

combination of properties provides advantages in electrical discharge machining fluids applications.

Typically, the Fischer-Tropsch gasoil fraction according to the present invention has very low levels of aromatics, naphthenic paraffins (also referred to as naphthenics) and impurities. The low level of impurities, aromatics and naphthenics gives the Fischer-Tropsch gasoil fraction according to the present invention an improved odor compared to crude oil derived gasoil, even after dearomatization. While the presence of normal paraffins and mono-methyl branched isoparaffins (mono-methyl isoparaffins) may provide improved bio-degradability compared to other isoparaffins.

The Fischer-Tropsch gasoil fraction according to the present invention is a fraction of the full-range Fischer-Tropsch gasoil that is derived from a Fischer-Tropsch process. Full-range Fischer-Tropsch derived gasoil, herein also referred to as Fischer-Tropsch gasoil, is known in the art. By the term “Fischer-Tropsch -derived” is meant that the gasoil, is, or is derived from, a synthesis product of a Fischer-Tropsch process. In a Fischer-Tropsch process, synthesis gas is converted to a synthesis product. Synthesis gas or syngas is a mixture of predominantly hydrogen and carbon monoxide that is obtained by conversion of a hydrocarbonaceous feedstock. Suitable feedstocks include natural gas, crude oil, heavy oil fractions, coal, biomass or lignocellulosic biomass and lignite. A Fischer-Tropsch derived gasoil may also be referred to as a GTL (Gas-to-Liquids) gasoil. The Fischer-Tropsch gasoil is characterized as the product of a Fischer-Tropsch process wherein a synthesis gas, or mixture of predominantly hydrogen and carbon monoxide, is processed at elevated

temperature over a supported catalyst comprised of a Group VIII metal, or metals, e.g., cobalt, ruthenium, iron, etc. At least part of the Fischer-Tropsch product is contacted with hydrogen, at hydrocracking/ hydroisomerization conditions over a, preferably, bifunctional, catalyst, or catalyst containing a metal, or metals, hydrogenation component and an acidic oxide support component active in producing both hydrocracking and hydroisomerization reactions. A least part of the resulting hydrocracked/hydroisomerized Fischer-Tropsch product may be provided as the Fischer-Tropsch derived gasoil feedstock.

Fischer-Tropsch gasoils are different from crude oil-derived gasoils. Despite having a similar boiling point range, the specific molecular composition of the Fischer-Tropsch gasoils may allow for, amongst others, improved viscosity characteristics, improved pour point characteristics, improved density characteristics and in particular a combination of any of the aforementioned characteristics with specific desired flash point characteristics. For example, Fischer-Tropsch gasoils may combine a low volatility with a high flash point, whereas the viscosity of such Fischer-Tropsch gasoils may be lower than the viscosity of crude oil-derived gasoil feedstock having a similar volatility and flash point.

The different characteristics of the Fischer-Tropsch gasoils, compared to the crude oil-derived gasoils, are generally attributed to their particular isoparaffin to normal paraffin weight ratio (i/n ratio), relative amount of mono-methyl branched isoparaffins and the molecular weight distribution of the paraffins.

A particular advantage of the Fischer-Tropsch derived gasoils is that these gasoils are almost

colorless. Color as used herein is the Saybolt color as measured by its Saybolt number (ASTM D156: Standard Test Method for Saybolt Color of Petroleum Products). A high Saybolt number, +30, indicates colorless fluids, whereas lower Saybolt numbers, in particular below zero, indicate a discoloration. A Saybolt number lower than 25 already indicates the presence of a visually observable discoloration. Fischer-Tropsch gasoils typically have the highest Saybolt number, i.e. +30. The good color characteristics, together with the above mentioned improved viscosity, pour point, density and flash point characteristics make the Fischer-Tropsch derived gasoils highly suitable for electrical discharge machining fluids or oil applications.

It has now been found that it may be possible to meet specific requirements of particular applications of the Fischer-Tropsch derived gasoil by using a specific fraction of a Fischer-Tropsch gasoil, wherein the fraction has a more narrow boiling point range compared to the full-range Fischer-Tropsch gasoil. By fractionating the Fischer-Tropsch gasoil, isoparaffins and normal paraffins are distributed unevenly over the fractions and Fischer-Tropsch gasoil fractions may be obtained that have an i/n ratio different from the original Fischer-Tropsch gasoil. Also the relative amount of mono-methyl branched isoparaffins and the molecular weight distribution of the paraffins may be different. As a consequence the viscosity, pour point, density and flash point characteristics of the Fischer-Tropsch gasoil fractions may be changed, beyond the change that would be expected on the basis of a fractionation on the basis of boiling ranges alone.Fischer-Tropsch gasoil contain primarily isoparaffins, however they also contain normal

paraffins. Preferably, the Fischer-Tropsch gasoil fraction comprises more than 70 wt% of iso-paraffins, preferably more than 75 wt% of iso-paraffins.

A fraction of the Fischer Tropsch gasoil is a narrower boiling range distillation cut of the Fischer Tropsch gasoil.

According to the present invention, the Fischer-Tropsch gasoil fraction has an initial boiling point of at least 200°C and a final boiling point of at most 300°C, at atmospheric conditions. Suitably, the Fischer-Tropsch gasoil fraction has an initial boiling point of at least 210°C, more preferably at least 225°C, at atmospheric conditions.

The Fischer-Tropsch gasoil fraction preferably has a final boiling point of at most 290°C, at atmospheric conditions. Further, the Fischer-Tropsch gasoil fraction preferably has a final boiling point of at most 263°C, at atmospheric conditions. By excluding lower boiling hydrocarbons that normally considered to be part of a full-range Fischer-Tropsch gasoil the fraction may have an advantageous lower volatility and a higher boiling point and flash point. By excluding higher boiling hydrocarbons that normally considered to be part of a full-range Fischer-Tropsch gasoil the viscosity of the fraction may be advantageously lowered.

A preferred Fischer-Tropsch gasoil fraction has an initial boiling point of at least 225°C and a final boiling point of at most 263°C, at atmospheric conditions.

By boiling points at atmospheric conditions is meant atmospheric boiling points, which boiling points are determined by ASTM D86.

Preferably, the Fischer-Tropsch gasoil fraction has a T10 vol% boiling point in the range of from 224 to 242°C, more preferably of from 227 to 239°C, most preferably of from 230 to 236°C and a T90 vol% boiling point in the range of from 244 to 262°C, preferably of from 247 to 259°C and more preferably of from 2250 to 256°C.

T10 vol% boiling point is the temperature corresponding to the atmospheric boiling point at which a cumulative amount of 10 vol% of the product is recovered. Similarly, T90 vol% boiling point is the temperature corresponding to the atmospheric boiling point at which a cumulative amount of 90vol% of the product is recovered. The atmospheric distillation method ASTM D86 is used to determine the level of recovery.

The Fischer-Tropsch gasoil fraction comprises preferably paraffins having from 10 to 17 carbon atoms; the Fischer-Tropsch paraffin gasoil fraction comprises preferably at least 70 wt%, more preferably at least 85 wt%, more preferably at least 90 wt%, more preferably at least 95 wt%, and most preferably at least 98 wt% of Fischer-Tropsch derived paraffins having 10 to 17 carbon atoms based on the total amount of Fischer-Tropsch derived paraffins.

Further, the Fischer-Tropsch gasoil fraction preferably has a density at 15°C according to ASTM D4052 in the range of from 759 kg/m^3 to 765 kg/m^3, more preferably of from 760 kg/m^3 to 764 kg/m^3, and most preferably of from 761 kg/m^3 to 763 kg/m^3.

Suitably, the kinematic viscosity at 25°C according to ASTM D445 is in the range of from 2.3 to 2.9 cSt, preferably of from 2.4 cSt to 2.8 cSt, and more preferably of from 2.5 cSt to 2.7 cSt.

Preferably, the flash point the Fischer-Tropsch gasoil fraction has a flash point according to ASTM D93 of at least 88 °C, preferably in the range of from 88 to 102 °C, more preferably of from 91 to 99 °C, and most preferably of from 92 to 98 °C.

The Fischer-Tropsch gasoil fraction has a smoke point according to ASTM D1322 of more than 50 mm.

Typically, the Fischer-Tropsch gasoil fraction according to the present invention comprises less than 500 ppm aromatics, preferably less than 360 ppm aromatics, more preferably less than 300 ppm aromatics, less than 3 ppm sulphur, preferably less than 1 ppm sulphur, more preferably less than 0.2 ppm sulphur, less than 1 ppm nitrogen and less than 4wt% naphthenics, preferably less than 3 wt% and more preferably less than 2.5 wt% naphthenics.

Further, the Fischer-Tropsch gasoil fraction preferably comprises less than 0.1 wt% polycyclic aromatic hydrocarbons, more preferably less than 25 ppm polycyclic aromatic hydrocarbons and most preferably less than 1 ppm polycyclic aromatic hydrocarbons.

The amount of isoparaffins is suitably more than 70 wt% based on the total amount of paraffins having from 10 to 17 carbon atoms, preferably more than 75 wt%.

Further, the Fischer-Tropsch gasoil fraction may comprise normal paraffins, also referred to as n-paraffins, and cyclo-alkanes.

The Fischer-Tropsch gasoil fraction preferably has an isoparaffin to normal paraffin weight ratio (also referred to as i/n ratio) of in the range of from 3.0 to 4.0. This i/n ratio may advantageously affect amongst others the viscosity of the Fischer-Tropsch gasoil fraction. The concentration of isoparaffin may be high

enough to benefit a lower overall viscosity. At the same time the significant amount of normal paraffins may benefit the bio-degradability.

Preferably, the Fischer-Tropsch gasoil fraction comprises in the range of from 30 to 60 wt%, more preferably of from 40 to 50wt%, of mono-methyl branched isoparaffins, based on the total weight of isoparaffins in the Fischer-Tropsch gasoil fraction. Mono-methyl branched isoparaffins exhibit desirable bio degradation characteristic compared to other isoparaffins. A relative high concentration of mono-methyl isoparaffins to other isoparaffins may advantageously affect amongst others the bio degradation characteristics of the Fischer-Tropsch gasoil fractions. A higher relative concentration of mono-methyl isoparaffin to other isoparaffins may provide the Fischer-Tropsch gasoil fraction with bio degradation characteristics beyond the bio degradation characteristics of the Fischer-Tropsch gasoil.

The Fischer-Tropsch gasoil fraction has a much narrower boiling range compared to the Fischer-Tropsch gasoil, allowing for its use in many applications. Due to its relative highly paraffinic nature and relative low levels of naphthenic and aromatic components and in addition the relative low levels of impurities, the Fischer-Tropsch gasoil fraction of the invention incorporates several technical benefits over conventional, crude oil derived fluids. Compared to existing isoparaffinic fluids currently on the market, the Fischer-Tropsch gasoil fraction has a more desirable mix of isoparaffins and n-paraffins. While competitive isoparaffinic fluids predominantly contain isoparaffins, and especially the higher boiling isoparaffins, including naphthenic paraffins, this Fischer-Tropsch gasoil fraction

of the invention contains isoparaffins and n-paraffins, while containing very minor amounts of naphthenic paraffins.

When used in for instance electrical discharge machining fluids applications the low odor and relatively low toxicity, due to the low aromatic content, are a distinct benefit as well as the improved bio degradation due to the high concentration of normal paraffins and mono-methyl isoparaffins. The Fischer-Tropsch gasoil fraction relatively low vapour pressure, odour, and high flash point will improve health and safety of workers, while its relatively low viscosity will ensure efficient and economic machining, flushing, pumping and wetting. The high oxidation stability of the Fischer-Tropsch gasoil fraction may increase the lifetime of the electrical discharge machining fluids considerably. A high flash point is desirable for safety reasons. Where prior art gasoils used for these applications suffered from an undesired high viscosity when using a high flash point gasoil, the Fischer-Tropsch gasoil fraction of the present invention having its specific composition and branching provides a high flash point while maintaining a viscosity that is relatively low compared to prior art isoparaffinic fluids, at same flash point levels. The combination of having a low viscosity and at the same time a relatively high flash point may find its benefits in electrical discharge machining fluids applications.

The preparation of the Fischer-Tropsch gasoil feedstock used as a basis for the Fischer-Tropsch gasoil fraction of the present invention has been described in e.g. WO02/070628 and WO-A-9934917 (in particular the process as described in Example VII of WO-A-9934917, using the catalyst of Example III of WO-A-9934917), both

of which are hereby incorporated by reference. As mentioned above these Fischer-Tropsch derived gasoil feedstocks have a different molecular composition and have significantly different properties compared to crude oil-derived gasoil feedstock. Therefore, Fischer-Tropsch derived gasoil feedstocks can be clearly distinguished from crude oil-derived gasoil feedstocks.

In a further aspect, the present invention provides a composition comprising a Fischer-Tropsch derived gasoil fraction according the invention. One particularly preferred composition is electrical discharge machining fluid. The Fischer-Tropsch gasoil fraction may be used alone or in combination with other compounds in the composition. Other compounds that are used in combination with the Fischer-Tropsch gasoil fraction include additives for functional fluid formulations such as, but are not limited to, corrosion and rheology control products, emulsifiers and wetting agents, borehole stabilizers, high pressure and anti-wear additives, de- and anti-foaming agents, pour point depressants, and antioxidants. Preferably, the other compounds comprise one or more compounds of corrosion and rheology control products, emulsifiers and wetting agents, borehole stabilizers, high pressure and anti-wear additives, de- and anti-foaming agents, pour point depressants, and antioxidants.

In another aspect, the invention provides for the use of the Fischer-Tropsch gasoil fraction in various applications. The Fischer-Tropsch gasoil fraction may be used alone or in combination with other compounds. Typically, Fischer-Tropsch gasoil fraction may be used in many areas, for instance oil and gas exploration and production, process oils, agro chemicals, process

chemicals, construction industry, food and related industries, paper, textile and leather, and various household and consumer products. Other compounds that are used in combination with the Fischer-Tropsch gasoil fraction include additives for functional fluid formulations such as, but are not limited to, corrosion and rheology control products, emulsifiers and wetting agents, borehole stabilizers, high pressure and anti-wear additives, de- and anti-foaming agents, pour point depressants, and antioxidants.

Preferred applications using the Fischer-Tropsch gasoil fraction according to the present invention include, but is not limited to, drilling fluids, heating fuels or oil, lamp oil, barbeque lighters, concrete demoulding, pesticide spray oils, paints and coatings, personal care and cosmetics, consumer goods, pharmaceuticals, industrial and institutional cleaning, adhesives, inks, air fresheners, sealants, water treatment, cleaners, polishes, car dewaxers, electric discharge machining, transformer oils, process oil, process chemicals, silicone mastic, two stroke motor cycle oil, metal cleaning, dry cleaning, lubricants, metal work fluid, aluminum roll oil, explosives, chlorinated paraffins, heat setting printing inks, Timber treatment, polymer processing oils, rust prevention oils, shock absorbers, greenhouse fuels, fracturing fluids and fuel additives formulations.

In particular the invention provides the use of a Fischer-Tropsch gasoil fraction according to the invention or a composition comprising such Fischer-Tropsch gasoil fraction in an electrical discharge machining fluid.

The present invention is described below with reference to the following Examples, which are not intended to limit the scope of the present invention in any way.

Examples

Example 1

Preparation of a Fischer-Tropsch gasoil fraction having an initial boiling point of 225°C and a final boiling point of 263°C

A Fischer-Tropsch product was prepared in a process similar to the process as described in Example VII of WO-A-9934917, using the catalyst of Example III of WO-A-9934917. The C_5+ fraction (liquid at ambient conditions) of the product thus obtained was continuously fed to a hydrocracking step (step (a)). The C_5+ fraction contained about 60 wt% C_{30}+ product. The ratio C_{60}+/C_{30}+ was about 0.55. In the hydrocracking step the fraction was contacted with a hydrocracking catalyst of Example 1 of EP-A-532118. The effluent of step (a) was continuously distilled under vacuum to give light products, fuels and a residue "R" boiling from 370 °C and above. The conversion of the product boiling above 370 °C into product boiling below 370 °C was between 45 and 55 wt%. The residue “R” was recycled to step (a). The conditions in the hydrocracking step (a) were: a fresh feed Weight Hourly Space Velocity (WHSV) of 0.8 kg/l.h, recycle feed WHSV of 0.4 kg/l.h, hydrogen gas rate = 1000 Nl/kg, total pressure = 40 bar, and a reactor temperature in the range of from 330 °C to 340 °C.

The obtained fuels fraction ($C5^+$- 370°C) was continuously distilled to give an approximate gasoil fraction yield as given in Table 1.

The physical properties are given in Table 2.

Table 1

Fischer-Tropsch gasoil fraction	
Yield ASTM D2892 (wt%)	28

Table 2

Fischer-Tropsch gasoil fraction	
Kinematic viscosity at 25°C According to ASTM D445 [mm^2/s]	2.6
content of aromatics According to SMS 2728 [mg/kg]	<200
content of n-paraffins According to GCxGC - internal testing methodology [wt%]	21.2
content of isoparaffins According to GCxGC - internal testing methodology [wt%]	77
Density at 15°C According ASTM D4052 [kg/m^3]	762
T10 vol.% boiling point According to ASTM D86 [°C]	233
T90 vol.% boiling point According to ASTM D86 [°C]	253
Smoke point [mm]	>50
Carbon number range paraffins	10-17
Flash point according to ASTM D93 [°C]	95

content of monomethyl isoparaffins According to GCxGC – internal testing methodology [wt%, based on total isoparaffins]	45
Visual Appearance	Clear and bright

C L A I M S

1. Fischer-Tropsch gasoil fraction having an initial boiling point of at least 200°C and a final boiling point of at most 300°C.

2. Fischer-Tropsch gasoil fraction according to claim 1, having an initial boiling point of at least 210°C.

3. Fischer-Tropsch gasoil fraction according to claim 1 or 2, having a final boiling point of at most 290°C.

4. Fischer-Tropsch gasoil fraction according to any one of claims 1 to 3, having a kinematic viscosity at 25°C according to ASTM D445 in the range of from 2.3 to 2.9 cSt.

5. Fischer-Tropsch gasoil fraction according to any one of claims 1 to 4, having a flash point according to ASTM D93 of at least 88°C.

6. Fischer-Tropsch gasoil fraction according to any one of claims 1 to 5, containing no more than 4 wt% of naphthenic paraffins, based on the Fischer-Tropsch gasoil fraction.

7. Fischer-Tropsch gasoil fraction according to any one of claims 1 to 6, containing isoparaffins and normal paraffins in a weight ratio of isoparaffins over normal paraffins in the range of from 3.0 to 4.0.

8. Composition comprising a Fischer-Tropsch gasoil fraction according to any one of claims 1 to 7.

9. Composition according to claim 8, wherein the composition is an electrical discharge machining fluid.

10. Use of a Fischer-Tropsch gasoil fraction as defined according to one of more of claims 1 to 7 or a composition comprising such Fischer-Tropsch gasoil fraction in an electrical discharge machining fluid.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2015/061514

A. CLASSIFICATION OF SUBJECT MATTER
INV. C10L1/04 C10M105/04
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C10G C10L C10M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2009/111723 A1 (SHIBATA JUNICHI [JP] ET AL) 30 April 2009 (2009-04-30) paragraphs [0047], [0051], [0069]; table 1.3	1-10
X	WO 02/070628 A2 (SHELL INT RESEARCH [NL]; HOEK AREND [NL]; SENDEN MATHIJS MARIA GERARDU) 12 September 2002 (2002-09-12) cited in the application page 1, line 1 - line 5 page 4, line 33 - page 5, line 8	1-9

-/--

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
10 August 2015	17/08/2015

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Chau, Thoi Dai

1

Form PCT/ISA/210 (second sheet) (April 2005)

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	SAMANEH HAJIPOUR ET AL: "Uncertainty analysis applied to thermodynamic models and process design 1. Pure components", FLUID PHASE EQUILIBRIA, ELSEVIER, AMSTERDAM, NL, vol. 307, no. 1, 21 May 2011 (2011-05-21), pages 78-94, XP028231010, ISSN: 0378-3812, DOI: 10.1016/J.FLUID.2011.05.014 [retrieved on 2011-05-27] Appendix A; page 92 -----	1-3,8,9

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2015/061514

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2009111723 A1	30-04-2009	EP 2006365 A2	24-12-2008
		US 2009111723 A1	30-04-2009
		WO 2007114505 A1	11-10-2007
WO 02070628 A2	12-09-2002	AR 032931 A1	03-12-2003
		AT 368095 T	15-08-2007
		AU 2002256642 B2	05-10-2006
		BR 0207894 A	22-06-2004
		CA 2440048 A1	12-09-2002
		DE 60221399 T2	17-04-2008
		DK 1412459 T3	26-11-2007
		JP 4084664 B2	30-04-2008
		JP 2004536894 A	09-12-2004
		KR 20030080077 A	10-10-2003
		MX PA03007983 A	04-12-2003
		MY 129748 A	30-04-2007
		NO 20033902 A	04-11-2003
		NZ 527944 A	31-03-2006
		US 2004074810 A1	22-04-2004
		WO 02070628 A2	12-09-2002